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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of OH and HO_2 concentrations during the MCMA-2006 field campaign – Part 1: Deployment of the Indiana University laser-induced fluorescence instrument" *by* S. Dusanter et al.

S. Dusanter et al.

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We are grateful to the anonymous Referee 2 and Dr. Sasha Madronich for the valuable comments and suggestions which helped us to improve the manuscript. For clarity, the major and minor comments are reproduced below with a bold font, followed by our replies. Suggested technical corrections have been done and are not included in the following reply.

Comments from Anonymous Referee 2

1) P. 13705, lines 25-29: It seems premature to predict that "strong evidence that

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the detected signal arises solely from the OH radical" will be found when these tests have not yet been performed. If there is reason to believe that this evidence will be strong from preliminary tests, then this should be stated and the reasons for the "strong evidence" wording stated. Otherwise, simply state that these proposed tests will be done at a later time and will provide quantitative evidence regarding possible interferences or lack thereof.

The manuscript has been modified as the following:

"The spectral properties of the fluorescing species, excitation spectrum and lifetime of the excited state, will be monitored using an automated sequence. The recorded parameters will be compared to that expected for the OH radical to provide quantitative evidences that the detected signal arises from the OH radical solely."

2) P. 13706, lines 5-10: What, if any, were the concentration ranges tested by Ren et al. for the interferences? Is there a quantitative limit reported? Are the reported concentrations of these species in MCMA within these limits?

The manuscript has been revised to include the information mentioned above. The text has been modified as the following:

"Ren et al (Ren et al., 2004) investigated potential photolytic interferences from HONO (up to 5 ppb), H_2O_2 (up to 120 ppb), HNO_3 (up to 50 ppb) and acetone (up to 200 ppm) on the GTHOS instrument and concluded that none of these species were able to generate significant interferences. Note that the concentrations used during those tests were higher than that observed during MCMA-2006."

3) P. 13707, lines 1-2: Describe briefly (more explicitly) what "a change in the efficiency of the chemical modulation" implies.

To clarify this assertion, the following information has been added in the text:

"However, a change in the chemical modulation efficiency could indicate the production of OH from a non-photolytic source. The chemical modulation efficiency can be

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defined as one minus the ratio between the OH signal remaining after reaction with the chemical reagent and the OH signal monitored without reagent flowing. The chemical modulation efficiency depends on instrumental parameters such as the concentration of the chemical reagent (C_3F_6) inside the sampling cell, the internal pressure and the transit time between the sampling point and the detection zone. This parameter can be characterized under the working conditions of the FAGE apparatus for various concentrations of reagent using an interference-free source of OH radicals such as the photolysis of water-vapor. During ambient measurements, if OH is produced in the sampling cell by decomposition of unstable species, the chemical modulation efficiency should appear lower than that observed during laboratory measurements."

4) P. 13710, lines 4-9: The information detailing the variability in the detection limit seems very key, especially based on the "observed minimum detectable" reaching as high as 2.6 x 10^6 molec cm^{-3}. Some reassurance to the reader that these periods of non-ideal detection limits were factored into the reported data and quantifying the proportion of data coverage that was affected by the noise would be highly valuable. Obviously many measured concentrations during the MCMA-2006 campaign were significantly above 2.6 x 10^6 molec cm^{-3}, but there are a number of reported data points that are at or below this detection limit.

An additional table has been added as Table 2 in the manuscript to display information about the variability of the limit of detection and the proportion of data above the limit of detection. References to this table have been added in the text (section 3.2: HO_x measurements). In addition, a red line has been added in Figs. 9-10 to display the daily-averaged detection limit.

5) P. 13712, lines 2-3: The reported OH "asymmetric profile with higher concentrations measured at this site during the morning hours" is not clear from Fig. 11. Perhaps it would be more fitting to report that on days where OH exceeded 10^7 molec cm^{-3} that this is the case? Similarly, the statement on line 5 that "high levels of OH are clearly observed" is not as clear to me. The concentrations on

March 15 look higher than those on March 16, but there is also missing data from the morning hours. Perhaps another faint line marking the local noon on the figure would help.

The OH profile displayed in Fig. 11 is slightly asymmetric compared to the J(O^1D) profile with higher concentrations measured before 1pm. However, this difference is not statistically significant and the statement about an asymmetric profile has been withdrawn from the manuscript. Instead, we emphasize the observation of high concentrations of both OH and HO_2 before noon on several days in section 3.2 of the revised manuscript. As suggested by the referee, lines marking local noon have been added in Figures 9 and 10.

6) P. 13714, lines 11-12: The authors state that only data with NO > 8 ppb are shown in Fig. 14, but the figure looks as though there are points at lower [NO].

This point has been corrected in the text. The dataset included in Fig. 14 covers a range of NO mixing ratios from 2 to 200 ppb. This figure gathers all the HO_x concentrations measured before noon from 14 to 31 March.

Comments from Dr. Sasha Madronich

Major comments

1. The production of O_3 estimated from HO_2 measurements is grossly inconsistent with observed O_3 concentrations. This is shown in Fig. 16: Integrating PO_3 in the morning hours predicts an increase of [O_3] of about 200 ppb by noon, which is more than double the actual observed O_3 concentration. The discrepancy is even worse when RO_2 is considered, and with the correction to Eq. (9) noted in the associated short comment by E. Wood. This discrepancy is not a new find (e.g. Olson et al., J. Geophys. Res., 111, D10301, doi:10.1029/2005JD006617, 2006) but remains largely unresolved. The authors need to acknowledge and discuss this important problem, and specifi-

cally whether instrumental problems could have resulted in artificially high HO_2 measurements at high NO_x.

We agree that the instantaneous production of O_3 estimated from the HO_2 measurements is inconsistent with the observed O_3 concentrations, and we have added the following discussion of this issue to the manuscript in section 3.3:

"The instantaneous production of O_3 estimated from the HO_2 measurements described above appears to be inconsistent with the observed O_3 concentrations, and may suggest an interference with the measured concentrations of HO_2. However, while surface ozone concentrations [O_3] and instantaneous ozone production P(O_3) are strongly linked together, these two parameters are characterized by different temporal and spatial scales. Measured O_3 concentrations, which depend on the history of the air mass being sampled, reflect an integration of P(O_3) over a large spatial scale and a long timescale. The calculations of instantaneous ozone production presented here do not take these issues into account, which are critical in the conversion of P(O_3) into an amount of ozone eventually produced. In order to relate measured surface O_3 concentrations and calculated instantaneous P(O_3), one may assume that P(O_3) is uniform throughout the MCMA. However, this assumption may be unrealistic since instantaneous P(O_3) is governed by local chemistry and may vary with the spatial and temporal distribution of NO_x, VOCs and HO_x sources and sinks over the MCMA. In addition, surface O_3 concentrations depend on physical and meteorological processes such as dry deposition, vertical and horizontal mixing and changes in the Planetary Boundary Layer (PBL) height. Clearly additional measurements are needed to resolve this issue."

The referee suggests discussing instrumental problems that could have resulted in artificially high HO_2 measurements at high NO_x. We agree that this point should be discussed in more detail in this publication. Higher than expected HO_2 concentrations have been reported under high NO_x concentrations for MCMA-2003 (Sheehy et al., 2008) and other urban environments (Martinez et al., 2003; Ren et al., 2003; Kanaya et al., 2007). Elevated concentrations of HO_2 reported for MCMA-2006 are consistent

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with the abovementioned studies. Several reasons can explain such discrepancy: (i) Instrumental artifacts, (ii) unsuitable modeling approaches, (iii) misunderstood chemistry, (iv) impact of heterogeneous mixing. The potential for instrumental artifacts is discussed below while (ii), (iii) and (iv) will be discussed in a separate publication (Dusanter et al., Measurements of OH and HO_2 Concentrations during the MCMA-2006 Field Campaign: Part 2 - Model Comparison and Radical Budget, in preparation). We have added the following discussion in the HO_x specificity section:

"Hydroperoxy radical measurements using FAGE are based on the rapid gas-phase titration of HO_2 by nitric oxide, which produces one molecule of OH per molecule of HO_2 reduced. The amount of OH produced during the titration step is then quantified by laser-induced fluorescence. As a consequence of the addition of high amounts of NO inside the sampling cell, secondary chemistry may lead to the production of spurious OH. These secondary reactions include the laser-photolysis of impurities present in the NO mixture and laser-photolysis of chemical species produced in the sampling cell. Artificial OH may also be generated by bimolecular reactions involving NO. Note that photo or thermal decomposition of chemical species formed in the atmosphere is unlikely to produce interferences during HO_2 measurements. If such interferences were present, their impact would be observed during OH measurements. Since HO_2 concentrations are generally much higher than OH (10 to 100 times), an interference observed at the ambient OH level would be insignificant at the ambient HO_2 level.

Tests performed during MCMA-2006 indicated that an interference was present during HO_2 measurements due to the addition of NO inside the sampling cell. We observed a signal showing a power dependence with the laser power and a linear dependence with the NO concentration, characteristic of a multi-photon process. This interference, probably caused by photolysis of unknown impurities in the NO mixture, has not been identified but was quantified during the MCMA campaign by performing zero-air tests. A flow-tube was attached to the sampling nozzle and the laser-generated OH was measured in clean air with NO flowing through the injector. Tests performed showed an excellent linearity between the detected signal and the NO flow. The net signal was normalized to 1-SCCM of NO and plotted against the laser power as shown in Fig. 6. The signal exhibits a clear dependence on the laser power, characterized by an exponential factor of 3.80 ± 0.07 (1σ , N=36 values). The exponential factor is higher than the expected quadratic dependence on laser power due to a two-photon process such as the O_3-water interference, and is likely the result of complex kinetics involving competing secondary reactions in the detection zone. Further laboratory tests will be performed to resolve this issue. However, the calibration curve shown in Fig. 6 allows quantification of the OH interference produced during HO_2 measurements, and this curve was used to correct the net HO_2 signal measured during the MCMA campaign. Corrections were in the range 5-60% on a daily average with the highest impact for days when HO_2 concentrations were low and a high laser power was used. In general, this correction was usually below 35%. The additional error due to this interference was included in the estimates of the precision of the HO_2 measurement.

The possibility of other potential interferences during tropospheric HO_2 measurements have been discussed in several publications (Stevens et al., 1994; Hard et al., 1995; Faloona et al., 2000; Martinez et al., 2003; Ren et al., 2004; Ren et al., 2006; Kanaya et al., 2007). One potential interference involves the conversion of ambient organic peroxy radicals (RO_2) to HO_2 inside the sampling cell. RO_2 radicals can react with NO leading to the production of HO_2 through a two-step mechanism (R5, R6):

(R5) RO_2 + NO –> RO + NO_2

(R6) RO + O_2 –> R'O + HO_2

The chemical reaction between RO_2 and NO leads to the formation of alkoxyl radicals (RO), which can decompose and/or react with oxygen to produce HO_2. However, numerical simulations (Stevens et al., 1994) and laboratory characterization (Ren et al., 2004) have shown that the rate of HO_2 formation from RO + O_2 is too slow under the reduced pressure conditions inside the FAGE cell to generate significant concentrations

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of HO_2 from ambient RO_2 relative to the transit time to the detection zone. Interference levels lower than 2% have been characterized by these authors.

Another potential interference involves thermal dissociation of peroxynitric acid (HO_2NO_2) and others peroxynitrates leading to the production of HO_2 radicals in the sampling cell. Previous studies have found that this type of interference is negligible under polluted conditions (100 ppb of NO_2) (Hard et al., 1995). In addition, thermal dissociation of HO_2NO_2 in a FAGE instrument was found to be negligible during aircraft measurements (Faloona et al., 2000). Production of OH from a chemical reaction between HO_2NO_2 and NO was recently proposed as another potential HO_2 interference (Kanaya et al., 2007). The authors argued that a conversion of 1% of HO_2NO_2 to OH would be enough to double the measured HO_2 signal since the HO_2NO_2/HO_2 ratio was as high as 100 during the IMPACT IV field campaign. On a median basis for MCMA-2006 between 8:40 and noon, measured HO_2 concentrations ranged from 6.5 to 13x10^7 cm^{-3} while model estimated concentrations of HNO_4 are in the range 5-10x10^8 cm^{-3} (Dusanter et al., Measurements of OH and HO_2 Concentrations during the MCMA-2006 Field Campaign: Part 2 - Model Comparison and Radical Budget, in preparation). Assuming a model-calculated [HNO_4] at noon of approximately 2x10^9 cm^{-3}, a HNO_4-to-OH conversion of 1% would lead to an estimated interference of 2x10^7 cm^{-3}, approximately 10% of the observed median HO_2 concentration measured at noon. A conversion efficiency of 3% would lead to an estimated interference of 6x10^7 cm^{-3}, which could account for 30% of the observed HO_2 signal. Although there have been no reported measurements of a reaction that converts peroxynitrates to OH under high NO_x conditions, additional studies are required to address this potential interference.

Intercomparison studies involving instruments based on different techniques for the measurement of HO_2 are sparse. HO_2 measurements were performed simultaneously by a FAGE and a MI-ESR (Matrix Isolation-Electron Spin Resonance) instruments during the BERLIOZ field campaign (Platt et al., 2002). A linear regression of the FAGE measurements vs. the MI-ESR measurements exhibits a slope of 1.03 ± 0.08 and an intercept of 0.15 ± 0.47 (R^2 = 0.94). Note that NO_x concentrations were in the range 2-16 ppb. An intercomparison between a FAGE and a CIMS instruments was performed at a rural site in Pennsylvania (Ren et al., 2003a) where ambient HO_2 concentrations were measured for 4 days under NO_x concentrations ranging from 4 to 7 ppb. A linear regression of the measured HO_2 concentrations resulted in a slope of 0.96 and a statistically insignificant intercept of 0.60 ppt (R^2 = 0.85). Recently, a FAGE instrument modified to measure RO_2 + HO_2 was compared to a MI-ESR instrument measuring the sum of peroxy radicals in the atmospheric simulation chamber SAPHIR (Fuchs et al., 2008). An excellent agreement was observed between the two techniques under low levels of NO_x. The three intercomparison studies mentioned above give confidence in ambient measurements of HO_2 using the FAGE instruments deployed in the field."

2. In the abstract, throughout the text and in the conclusion, the authors state that OH is highly buffered while HO_2 is highly variable. But very little evidence is presented to support this assertion. In Figs. 9 and 10, excursions in OH seem to be at least as large as those in HO_2. In Fig. 14, the variability in OH seems large compared to its mean value. In Fig. 13, the OH values range from -5e5 to 1.2e7 molec/cm^3 regardless of whether NO_x is high or low (HO_2 is not shown). And cursory inspection of Table 1 does not show remarkable consistency in OH, nor unusually high variability in HO_2. If the authors want to insist on this buffering aspect, they should provide solid quantitative statistical evidence for it.

We agree with the referee that the statement that OH is well buffered as described may not be a robust assertion. The manuscript has been revised accordingly.

3. The measurements of NO, NO_2, and O_3 concentrations and J(HONO) are not described, although they are used extensively in the interpretation of OH and HO_2 measurements. Were these measurements made by the authors? How? The data are absent from the official MILAGRO archive (NCAR Community Data Portal). Adequate description of these measurements is a sine qua non condition

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for archival publication in ACP.

Details about O_3, NO_x and J-values measurements have been added in the text as the following, and the error associated with their presence on the data portal has been corrected.

"Measurements of O_3, NO_x and J-values were performed on the roof of the building 32 at T0, collocated to IU-FAGE. O_3 was monitored using a commercial monitor (Teledyne 400E) based on UV absorption whose calibration was performed against a photometric O_3 calibrator (API, M401) before and after the MCMA field campaign. Measurements of NO_x (Thermo Environmental) were performed using a commercial monitor from RAMA based on chemiluminescence of NO_2. Uncertainty and detection limits for 10-min average are 10% (1σ) and 0.1 ppb (1σ) respectively for O_3, NO and NO_2 measurements. Photolysis frequencies for NO_2 –> NO + O(^{3}P), O_3 –> O(^{1}D) + O_2, HONO –> HO + NO, HCHO –> H + HCO and HCHO –> H_2 + CO were directly measured using a spectroradiometer as described for MCMA-2003 (Volkamer et al., 2007b). Uncertainties are estimated to be 25% for J(O^{1}D) and 15% for J(NO_2), J(HONO) and J(HCHO)."

Minor Comments

Eq. 5 seems incorrect. The rates (i.e. the inverse of the lifetimes) should be additive: 1/tau_tot = 1/tau_rad + sumk[q]. In Eq. 5 as written, for zero quencher ([q] = 0) the lifetime becomes infinite, which is unreasonable.

Eq.5 was incorrect and the manuscript has been corrected:

$$(\tau)^{-1} = (\tau_{rad})^{-1} + \Sigma k_{qi} q_i$$

The one-photon vs. two-photon argument (p. 13706, and Fig. 6) is not convincing. There are many reasons for which a specific scaling exponent could appear. This is seen in Fig. 6: The unidentified artifact leads to an exponent of 3.8, but certainly the authors would not argue that this results from a four-photon process. It is more likely the net result of complex kinetics involving competing

secondary reactions. Of course it is a bit unsettling that as much as 60% correction is required for an unidentified process.

The manuscript has been revised with the following: The changes appear in italic

"(i) In contrast to the detection of ambient OH, which is a one photon process, the detection of laser-generated OH requires two photons to successively produce and detect an OH molecule. *Providing that the OH absorption transition is not saturated*, the one-photon process will exhibit a linear dependence with the averaged laser power. *In addition, providing that the absorption transition of the interfering species is not saturated*, the two-photon process will exhibit a quadratic dependence *in the case of a direct production of OH (such as HONO –> OH + NO). If OH is generated during complex kinetics involving competing secondary reactions at the detection axis, a scaling exponent different than 2 may be observed.* In order to determine whether laser-generated OH is produced in the detection region, the OH concentration is successively measured at various laser powers, assuming that ambient OH concentrations do not vary significantly between the measurements."

13710/17: The belief that surrounding mountains limit the dispersion of pollutants is a myth which should not be propagated in the MILAGRO special issue. The mountains do contribute to complex local circulations (see de Foy et al., 2007, this issue).

This has been corrected in the manuscript.

13713/4-23: The discussion of which photolysis frequency provides the best proxy for OH is weak. All of the J values are going to be highly correlated, with only slight deviations due to differences in predominant wavelengths. Furthermore, the effect on OH will be far more sensitive to variations in photolytic precursor concentrations than photolysis frequencies. On lines 12, 13 it is claimed that OH correlates better with J(HONO) than J(O_3->O^1D), but no evidence is given; the literature cited refers to other locations and to J(NO_2), so it does not

provide support for this claim. Speculations, e.g. that the non-zero intercept of Fig. 13 arises from higher morning HONO concentrations (lines 17-20) seem without basis. The buffering argument (lines 20-23) is also suspect, since the variability in OH is so large even at constant J(HONO).

As suggested, we have revised the manuscript to include a figure with correlations of both J(HONO) and J(O^{1}D) with measured OH concentrations. Although it has been suggested that there should be a stronger correlation of OH with J(HONO), the observed correlation for MCMA-2006 is not significantly stronger than that with J(O^{1}D). As before, the suggestion that OH is highly buffered in this environment has been removed, as have the speculation on the source of the non-zero intercept in the correlation plots. The manuscript has been revised in section 3.2 with the following paragraph (changes in italics):

"Photolysis of O_3 at short wavelengths and the subsequent reaction of the photoproduct O(^{1}D) with water-vapor (R1-R2) is the major source of RO_x (OH + HO_2 + RO_2) radicals in the remote-rural troposphere and J(O^{1}D) can be considered as an indicator for the total photolytic production of odd hydrogen radicals. However, photolysis of other oxygenated species such as HONO, glyoxal, methylglyoxal and other dicarbonyl species can also contribute to the RO_x production in urban environments. The contribution of these species to the production of RO_x has been found to be important relative to O_3 photolysis in the MCMA (Volkamer et al., 2007). Note that like HONO, these species are photolyzed at wavelengths longer than 330-nm, and as a result J(HONO) is expected to be a better proxy than J(O^{1}D) to describe the total photolytic production of RO_x in this environment. *However, the observed correlation of the measured OH concentration with J(HONO) is not significantly better than the observed correlation between OH and J(O^{1}D). Fig. 13 displays the correlation plots between measured OH and J(HONO) and J(O^{1}D) that illustrates the OH dependence on the photolytic production of radicals in MCMA-2006. The low correlation coefficient (R^2 = 0.199 for J(HONO), R^2 = 0.163 for J(O^{1}D)) indicates that less than 20% of the variance of OH*

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can be explained by variations in J(HONO) or J(O^1D). A large part of this variance can be attributed to the OH measurement precision and to a lesser extent to the variability of the atmospheric chemical composition (HONO, dicarbonyl species, O_3, NO) for similar J values. Fig. 13 also displays OH measurements performed under high and low NO_x conditions."

13714/5-16: The normalizations need to be made much more clear. Giving the actual equations may be useful. As currently written, it seems that OH(normalized,t) = OH(t) * Jave/J(t) while HO_x(normalized,t) = HO_x(t) * HONOave/HONO(t). However, I think the more likely formulation would be: OH(normalized,t) = OH(t) * Rave/R(t) where R(t) = J(t)*HONO(t)

The normalization applied to the measured OH and HO_2 concentrations was the same as suggested. In order to clarify this point in the manuscript, we modified the text and included the following equation as Equation 8.

$[HO_x]_{t,normalized}$ = $[HO_x]_t$ x $(J(HONO)_{avg}$ x $[HONO]_{avg})$ / $(J(HONO)_t$ x $[HONO]_t)$

13714/16: Is it really as expected? I think model calculations would show a much steeper decrease of HO_2 for large NO (e.g. > 30 ppb).

The referee is right about the steeper decrease of HO_2 predicted by model calculations. In an upcoming publications (Dusanter et al., Measurements of OH and HO_2 Concentrations during the MCMA-2006 Field Campaign: Part 2 - Model Comparison and Radical Budget, in preparation), we show that the model-calculated HO_2/OH ratio exhibit a steeper decrease than the measured ratio, which is linked to the HO_2-NO dependence. However, in this publication, we just intended to show that the measured HO_x concentrations were decreasing when NO was increasing. This general behavior is expected for a NO_x saturated environment. In order to clarify this point in the manuscript, the text in section 3.2 has been modified with the following:

"As can be seen in Fig. 14, both OH and HO_2 decrease with increasing NO. A decrease of both, OH and HO_2, is the expected qualitative behavior in a NO_x saturated environment. HO_2 decreases since NO shifts the partitioning of HO_x towards OH. OH also decreases as the result of an OH loss rate from OH + NO_2 that is higher than the OH production rate from HO_2 + NO. However, the observed decrease in OH and HO_2 with increasing NO is not as steep as expected. This point will be discussed in a companion paper (Dusanter et al., "Measurements of OH and HO_2 Concentrations during the MCMA-2006 Field Campaign: Part 2 - Model Comparison and Radical Budget", in preparation)."

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